SYNOPSIS

1. TITLE OF THE SYNOPSIS

"SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF THIOL-CAPPED SILVER AND GOLD NANOPARTICLES"

2. INTRODUCTION

A fundamental goal of materials science is the design and synthesis of materials with customized shape and size. This goal underpins the growing interest in the fabrication of intelligent and complex materials such as artificial bones, teeth and cartilage, nanowires for electronic circuitry, shape memory alloys, and plasmon based sensors.

The mechanisms supporting these synthetic methods have evolved empirically and there is no accepted mechanism to explain how shape control works, particularly in a material such as gold where the surface free energies and chemistry of the major facets are similar. It is perhaps salient to point out that gold nanoparticles have been synthesized for over 2000 years in whole range of media including glasses, salt matrices, polymers, the gas phase and in water-invariably these methods have resulted in the formation of spheres. It is only in the past decade that significant progress towards non-spherical nanoparticles synthesis has been achieved. In this tutorial review we summaries some of the emerging protocols for shape control of metal nanocrystals, and we examine some of the mechanisms currently proposed to help explain this important advance in materials science. Lofton and Sigmund provided the first such review in 2005,[1] focusing on the crystallographic aspects of shape control, including twinning. Here the focus is on how different chemical environments appear to promote the growth of different shapes, from platonic solids through to rods and branched metal nanocrystals.

Noble metal (gold, silver) nanoclusters (NCs), collected of a small amount of approximately a hundred atoms, are a new type of luminescent nanomaterials that have attracted a great interests recently.[2-5]

Reduction of solution,[6-8] thermal,[9] electrochemical,[10] and sonochemical decomposition,[11] microwave-assisted synthesis,[12] and green chemistry[13-16] are available for the synthesis of metal nanoparticles. Green chemistry synthesis approaches must be designed for reduced environmental impact, waste reduction, process safety, materials, and energy efficiency. Using plants in the greensynthesis of gold and silver nanoparticles, has received more attention as suitable alternative to chemical procedures and physical methods.

Nanomaterials preferred physiochemical properties which needed for targeted applications. It is important to correlate the composition and structure of the nanoclusters with their properties for application design.[17] Most of the synthesized gold and silver NPs are currently uses in biological applicatios from novel biosensing devices[18-19] to cancer therapy,[20] being thus compulsory that the synthesized NPs are water-soluble and easily functionlized for surface chemistry fine –tuning.

Gold nanoparticles stabilized by thiolates, often referred as monolayer protected clusters (MPC), have attracted extensive research interests due to their rich optical and other physiochemical properties.[21-23]

3. REVEIW OF THE EARLIAR WORK

Large amount of work is carried out for synthesis, characterization of nanomaterials and their applications in numerous fields. There is much current interest in metal nanoparticles due to their fascinating electronic and optical properties and potential application in the areas of catalysis,[24] nonlinear optical devices,[25] electron microscopy markers,[26] DNA sequencing,[27] and the emerging area of plasmonics.[28]

Zhang *et al*.[29], have worked on "Fluorescence Intensity and Lifetime Cell Imaging with Luminescent Gold Nanoclusters" They have two types of water-soluble AuNCs which were stabilized with a monolayer composed of either mercaptosuccinic acid (MSA) or tiopronin thiolate ligands were synthesized by a chemical reduction reaction.

Tang *et al*.[30], have carried out dithiol ligand 2, 3-dimercaptopropanesulfonic (DMPS) acid has been employed to synthesize dithiol-protected Au clusters (DTCs). The structure and property of the AuDTCs are studied to probe two effects: the entropy gain of dithiol over

monothiol ligand protection and theconstraint to the formation of the thiol bridging surface bonding.

Structural and theoretical basis for ligand exchange on thiolate monolayer protected gold nanoclusters has been done by Heinecke *et al*.[31] The results are density functional theory calculations modeling both thiol and thiolate incoming ligands postulate a mechanistic pathway for thiol-based ligand exchange. The discrete modification of a small set of ligand binding sites suggests Au_{102} (p-MBA)$_{44}$ as a powerful platform for surface chemical engineering.

Monodisperse protein stabilized gold nanoparticales via a simple photochemical process has been studied by Housni *et al*.[32] The results show that synthesize not only monodispersed Ag NPs but also core–shell Ag–Au NPs with a discrete structure, which is significant because of the challenges associated with the creation of such materials, namely the propensity of metallic Ag to be oxidized by the presence of ionic Au.

Synthesis of silver nanoparticles from the aqueous extract of leaves of Ocimum sanctum for enhanced antibacterial activity has been done by Ramteke *et al*.[33] Synthesized NPs was found to be 18 nm, as confirmed by TEM. The qualitative assessment of reducing potential of leaf extract has also been carried out which indicated presence of significant amount of reducing entities.

Chen and co-workers have shown that two-dimensional gold nanoparticle networks cross-linked by biofunctional bridging linkers such as TBBT (4, 4'-thiobisbenzenethiol) may be achieved at the air-water interface.[34]

4. OBJECTIVE OF THE STUDY

The entire work has been studies under following chapters

1. Synthesis and characterization of thiol capped gold and silver nanoparticles.
2. To understand the factors affecting the biological activities of silver and gold nanoparticales.
3. To investigate the effect of thiol-capping agents on size and shape of the nanoparticle.

4. To study the antibacterial activity of thiol capped silver and gold nanoparticles.
5. To study the antioxidant activity of thiol-capped silver and gold nanoparticles.

5. NOTWORTHY CONTRIBUTION

Recently nanoscience has got tremendous interest in the field of science and technology due to its vast and vital application in each and every field of science. Recently, synthesis, characterization and photophysical properties of thioglycolic acid (TGA) and cysteine (Cys) capped-gold nanoparticles have been investigated. Further, bovine serum albumin (BSA) stabilized gold nanoparticles have been synthesized. Figure-1 and Figure-2 shows HRTEM images of TGA-capped and BSA stabilized gold nanoparticles.

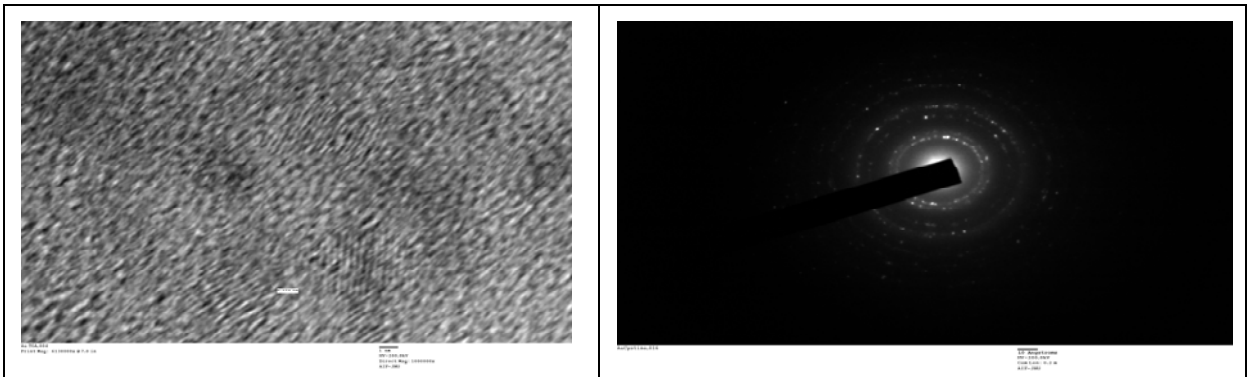

Fig.1 HRTEM image and SAED pattern of TGA-capped Gold Nanoparticle

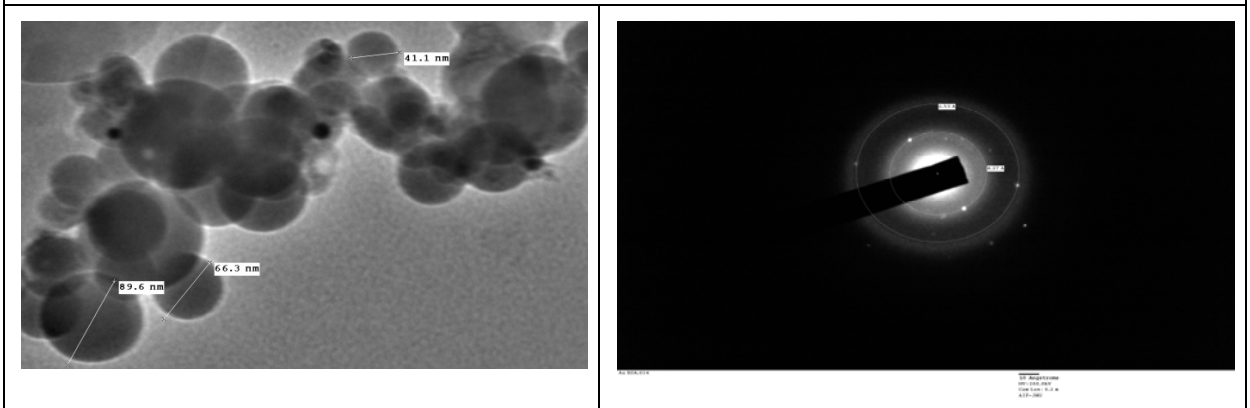

Fig.2: HRTEM image and SAED pattern of BSA-stabilised Gold Nanoparticle

6. PROPOSED METHODLOGY

The complete work will be done under following sections:

I. Synthesis and Characterization of Gold and Silver Nanoparticles

Method (1): Synthesis of Gold and Silver nanoparticles through citrate reduction method.

Gold and silver nanoparticles will be synthesized in a one-step aqueous preparation in which hydrogen tetrachloroaurate or silver nitrate is brought to boiling and reduced by rapidly adding sodium citrate.[35] Particle diameter can be tuned via citrate: $[AuCl_4]^{1-}$ /$AgNO_3$ stoichiometry.

1. In a 1 L round-bottom flask equipped with a condenser, heat 500 mL of 1 mM $HAuCl_4$/$AgNO_3$ solution to boiling point with vigorous stirring.
2. After refluxing for 10 min, rapidly add 50 mL of 40 mM of trisodium citrate to the stirring solution. The color should change from a pale yellow to a deep wine red/ colorless to yellow in case of sliver nanoparticles color.
3. Let the solution boil for 10 minutes.
4. Remove heat and continue to boil for an additional 15 minutes.
5. Remove stir bar and allow the solution to cool down to room temperature.
6. Filter through 0.8 μm membrane filter.

Method (2): Synthesis of Gold and Silver nanoparticles through microemulsion method.

Gold and Silver nanoparticles will be synthesized via microemulsion method using modified literature method.[35] Microemulsion is prepared using Cyclohexane, CTAB/TX-100 as surfactant, and hexanol as cosurfactant and aqueous solution of $HAuCl_4$/$AgNO_3$ and Sodium citrate. The molar ratio of CTAB/TX-100 to hexanol is maintained at 1:4. The

microemulsion containg trisodium citrate is added to microemulsion containing $HAuCl_4/AgNO_3$ and stirred. Then the nanoparticles are separated by centrifugation at 15,000 rpm for 1 hour. Then the particles washed with distilled water and alcohol and dried at 50°C for 12 hr.

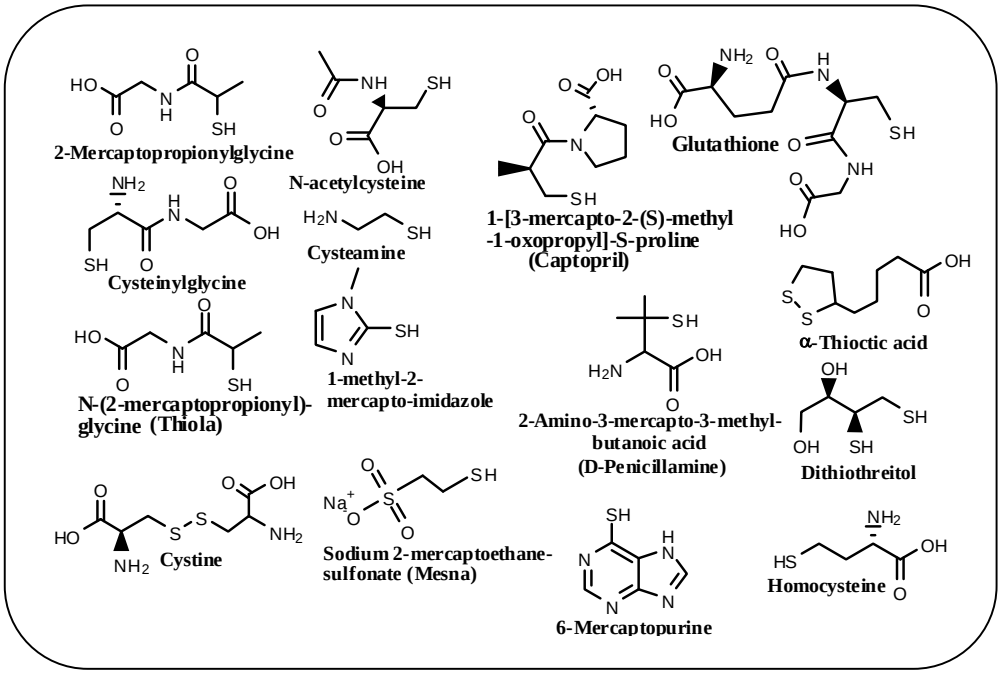

CHART-1

II. Effect of Thiol Capping on Size and Shape of the Gold and Silver Nanoparticles

This study deals with the synthesis of thiol-capped Ag and Au nanoparticles by borohydride reduction and spectroscopic identification of S Au interaction. It is proposed to study the interaction of thiol with gold nanoparticles in aqueous medium by employing UV–vis, Raman, NMR, and FT-IR spectroscopy. The shifting of gold plasmon resonance in the UV–vis spectra shows the stabilization of gold nanoparticles by thios (Chart-1). The disappearance of S-H stretching in both the IR and Raman spectra and the shifting of the NMR signals of the protons in close proximity to the metal center supported the existence of the S Au interaction in thiol-capped gold nanoparticles. It is expected that TEM images will show thiol-capped silver and gold nanoparticles as distinct and spherical entities as compared to free colloidal Ag and Au nanoparticles.

III. Antioxidant Activity of Thiol Capped Gold and Silver Nanoparticles

The use of nanomaterial in consumer products is rapidly expanding, in most studies nonomaterial are examined as isolated ingredients. However, consumer products such as foods cosmetics and dietary supplements are complex chemical matrixes. Therefore, interactions between nanomaterial and other components of the product must be investigated to ensure the products performance and safety. Silver nanomaterials are increasingly used in food packing and antimicrobial agents thiol-containing compounds, such as reduced glutathione (GSH), cysteine and dihydrolipoic acid are used as antioxidants in many consumer products. Therefore, it is proposed to investigate the interaction between silver and gold nanomaterials and thiol containing antioxidants. The selected Ag nanomaterial will be Ag coated with citrate, Ag coated with poly(vinylpyrolidine) and Au nanorods coated with Ag in a core shell structure, will be used for direct quenching of the 1,1-diphenyl-2-picrylhydrazil radical (DPPH). The effect of GSH and cysteine capped Ag and Au nanomaterials will be studied and expected to antioxidant activity at varying extent. In addition to this, the effect of the mixture of glutathione (GSH) and Au@Ag nanorod on the antioxidant activity will be studied at ambient temperature. Furthermore, the effect of Ag Au and Au@Ag nanorod on the antioxidant ability of GSH and cysteine will be studied. The work presented here will be demonstrated the importance of examining the chemical interactions between nanomaterial used in products and physiologically important antioxidants

IV. Antibacterial Activity of Thiol Capped Gold and Silver nanoparticles.

The antibacterial properties of thiol capped Ag and Au nanoparticles will be studied by applying the disc diffusion assay. The mechanism of antibacterial properties of glutathione coated, cysteine, dihydrolipic acid and other thiol capped silver and gold nanoparticles on the model gram negative and gram positive bacterial strains will be investigated. It is expected that the interference in bacterial replication will observed

for both cellular strains when exposed to GSH stabilized colloidal silver and gold in solution, and microbial activity of will studied when GSH coated AgNPs and AuNPs are (i) dispersed in colloidal suspension or (ii) grafted on thiol functionalised glass surface. The obtained results will confirm that the effect of dispersed GSH capped AgNPs and AuNPs (GSH AgNPs) on the Escherichia coli and Staphylococcus aureus. It is interesting to know that the penetration of the colloids in to the cytoplasm seem to easier though the cell wall of Escherichia Coli, with the subsequent local interaction of Ag and Au with cell components causing damages to the cell. Conversely, for staphylococcus aureus, since the thick peptidoglycan layer of the cell wall presents the penetration of the nanoparticles inside the cytoplasm, the antimicrobial effect is limited and seems related to the interaction with h the bacterial surface, experiments on GSH AgNPs grafted on glass allowed us to elucidate more precisely antibacterial mechanism, showing that the cation is reduced because of GSH coating and the limitation of the translational freedom of NPs.

7. EXPECTED OUTCOME OF THE PROPOSED WORK

The results of the entire work will results on:

(i) Understanding on the interaction of bare Ag and Au nanoparticles with thiolated ligands.

(ii) Large biological molecules such as proteins and enzymes are comprises of thiol functional amino acids (Cysteine). Therefore, the interaction of small thiolated molecule will provide information about the mechanism of bioconjugation of large biomolecules.

(iii) In vitro antioxidant activity of the thiol-capped silver and gold nanoparticle will be useful in further investigation in In vivo process.

(iv) The investigations on the antibacterial activity will be useful to understand the mechanism of biological activity of functionalized silver and gold nanoparticles.

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